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Aroyl Arenesulfonyl Peroxides. III. Thermal Decomposition of *p*-Chlorobenzoyl *p*-Toluenesulfonyl Peroxide.[1]

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p-Chlorobenzoyl *p*-toluenesulfonyl peroxide was synthesized. Its spontaneous decomposition in benzene or in carbon tetrachloride did not follow a first-order rate equation because of the rate acceleration due to *p*-toluenesulfonic acid produced. When powdery magnesium oxide was suspended in benzene, isomerization to *p*-chlorophenyl *p*-toluenesulfonyl carbonate was completely inhibited, and the rate followed a first-order equation. The products of decomposition (*p*-chlorobiphenyl, *p*-chlorobenzoic acid, *p*-toluenesulfonic acid, phenyl *p*-toluenesulfonate, *etc*) were accounted for in terms of initial formation of *p*-toluenesulfonyloxy and *p*-chlorobenzoyloxy radicals. *p*-Toluenesulfonyloxy radical was found to be a very effective hydrogen-abstractor with little tendency to add to benzene.

The synthesis and decomposition of benzoyl *p*-toluenesulfonyl peroxide was described in a previous paper.[2] Spontaneous decomposition in benzene was mainly an acid-catalyzed isomerization to phenyl *p*-toluenesulfonyl carbonate (42 mol%), but when powdery magnesium oxide was added the extent of isomerization decreased (22 mol%) and products ascribable to phenyl radical[2,3] were found (biphenyl, 44 mol%).

Such facile isomerization is undoubtedly due to the strong electron-withdrawing tendency of the *p*-toluenesulfonyl group. Thus, it is expected that a substituted benzoyl *p*-toluenesulfonyl peroxide with an electron-withdrawing substituent on the benzoyl group may undergo completely homolytic decomposition yielding benzoyloxy radical and *p*-toluenesulfonyloxy radical. As an example of such peroxide, *p*-chlorobenzoyl *p*-toluenesulfonyl peroxide (CTP) was synthesized and its decomposition was investigated.

Results and Discussion

p-Chlorobenzoyl *p*-toluenesulfonyl peroxide (CTP) was prepared by a reaction between *p*-toluenesulfonyl chloride, *p*-chloroperoxybenzoic acid and potassium hydroxide at −22°C.

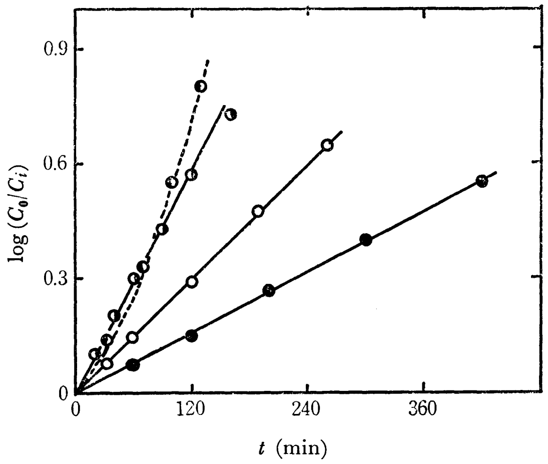

Fig. 1. Plots of $\log(C_0/C_i)$ *vs.* time for the decomposition of CTP in C_6H_6 in the presence of MgO.
● 40.0°C, ○ 45.0°C, ◑ 50.0°C, ◐ 45.0°C, in the absence of MgO

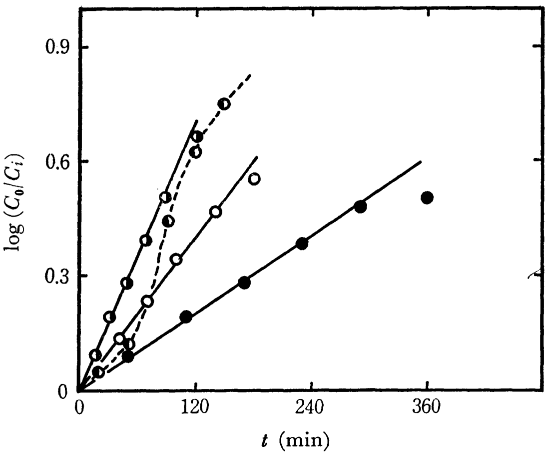

Fig. 2. Plots of $\log(C_0/C_i)$ *vs.* time for the decomposition of CTP in CCl_4 in the presence of MgO.
● 45.0°C, ○ 50.0°C, ◑ 55.0°C, ◑ 50.0°C, in the absence of MgO

Spontaneous decomposition of CTP without any additives in benzene or carbon tetrachloride did not follow a first-order rate equation because of the rate acceleration due to the *p*-toluenesulfonic acid produced. However, when powdery magnesium oxide was suspended in the medium, the decomposition followed an ordinary first-order rate equation. Figures 1 and 2 show the rate of decomposition. The rate constants obtained are listed in Table 1. Arrhenius plots are shown in Fig. 3. In benzene with

TABLE 1. FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF CTP

Temp. (°C)	in C_6H_6 + suspended MgO $k_1 \times 10^5$ (sec^{-1})	in CCl_4 + suspended MgO $k_1 \times 10^5$ (sec^{-1})
40.0	5.08	—
45.0	9.56	6.42
50.0	18.0	12.9
55.0	—	20.3
E_a (kcal/mol)	25.4	24.1
$\Delta S^{\ddagger}$ (e. u.)	+1.0	−3.9

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[1] Organic Sulfur Compounds. Part XXVII.

[2] R. Hisada, H. Minato, and M. Kobayashi, This Bulletin, **44**, 2541 (1971).

[3] R. Hisada, N. Kamigata, H. Minato, and M. Kobayashi, This Bulletin, **44**, 3475 (1971).

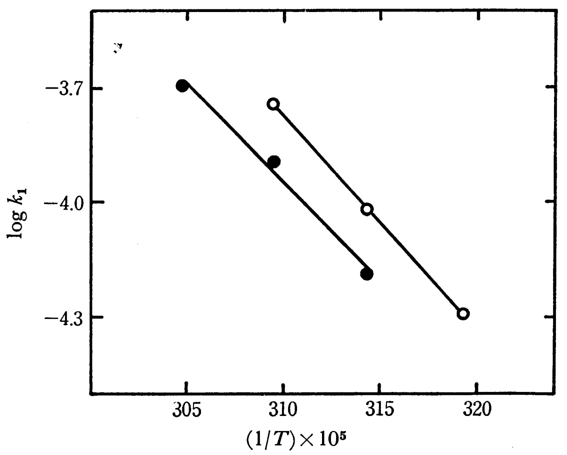


Fig. 3. Arrhenius plot for the decomposition of CTP.
○ in C_6H_6 + MgO, ● in CCl_4 + MgO

TABLE 2. DECOMPOSITION PRODUCTS OF CTP[a)]

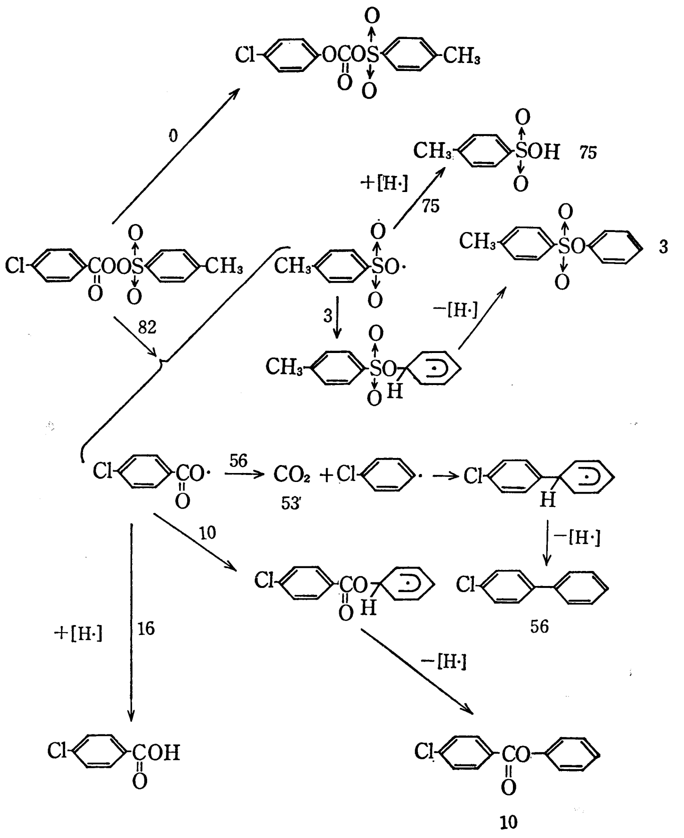
CTP (mmol)	5	4.5	2.5	3.5
Solvent	C_6H_6	C_6H_6	CCl_4	CCl_4
(m*l*)	50	150	120	170
Additives	—	MgO	—	MgO
(mmol)		45		35
Products (mol/mol of CTP)				
Carbon dioxide	—	0.53	0.45	0.60
p-Chlorophenyl *p*-toluenesulfonyl carbonate	0.42	0	0.12	0.07
p-Chlorobiphenyl	0.002	0.56	—	—
Biphenyl	trace	0.01	—	—
p-Dichlorobenzene	—	—	0.42	0.59
Hexachloroethane	—	—	0.19	0.38
p-Chlorobenzoic acid	0.27	0.16	0.26	0.09
p-Toluenesulfonic acid	0.48	0.75	0.71	0.37
Phenyl *p*-chlorobenzoate	0.07	0.10	—	—
p-Tolyl *p*-chlorobenzoate	trace	—	0.005	—
p-Chlorophenyl *p*-chlorobenzoate	0.01	—	trace	—
Phenyl *p*-toluenesulfonate	0.04	0.03	—	—
p-Chlorophenyl *p*-toluenesulfonate	trace	—	0.01	0.08
Chloride ion	—	—	0.06	>0.05
Accounted for				
p-Chlorophenyl- (%)	78	82	81	83
p-Toluenesulfonyloxy- (%)	94	78	84	52

a) Temperature, 45°C; Reaction time, 20 hr. These data are the average of two experiments. Experimental errors are within ±2%.

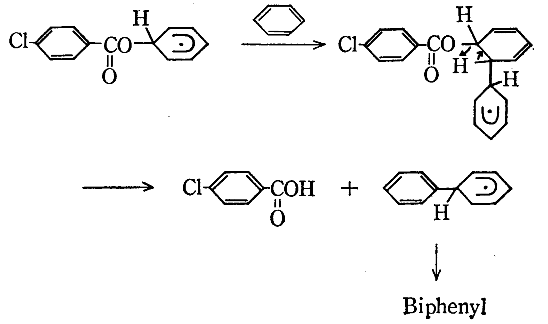
magnesium oxide, E_a was 25.5 kcal/mol and $\Delta S^{\neq}$ +1.0 e.u., whereas in carbon tetrachloride with magnesium oxide, E_a was 24.1 kcal/mol and $\Delta S^{\neq}$ −3.9 e.u.

Table 2 shows the products of decomposition of CTP in benzene and carbon tetrachloride in the absence and presence of magnesium oxide.

In the absence of magnesium oxide in benzene, isomerization to the mixed anhydride took place to a considerable extent (42 mol%), whereas in the presence of magnesium oxide isomerization was completely inhibited. The yields of various products in benzene can be summarized in the following scheme.



It is interesting to compare the behavior of three different radicals produced, namely, *p*-chlorophenyl, *p*-chlorobenzoyloxy and *p*-toluenesulfonyloxy radicals. Very reactive *p*-chlorophenyl radical almost exclusively adds to benzene molecules surrounding the radical (chlorobenzene was not detected), whereas the fate of *p*-chlorobenzoyloxy radical is 10 addition to benzene *versus* 16 hydrogen-abstraction from cyclohexadienyl radicals. *p*-Toluenesulfonyloxy radical must be a very effective hydrogen-abstractor, since its fate was 3 addition to benzene *versus* 75 hydrogen-abstraction from cyclohexadienyl radicals. The sulfonyloxy radical is stable enough to stay unreacted in the medium until it collides with cyclohexadienyl radicals (*p*-chlorophenyl-, *p*-chlorobenzoyloxy-, or *p*-toluenesulfonyloxycyclohexadienyl radicals.)



Decomposition of CTP in benzene with magnesium oxide produced unsubstituted biphenyl in 1.1 mol% yield. It was identified by gas chromatography, elution chromatography and infrared spectroscopy. A plausible mechanism of its formation is the above.

When CTP was decomposed in carbon tetrachloride, addition of magnesium oxide did not result in complete inhibition of rearrangement, and the mixed anhydride was produced in 7.4 mol% yield. However, formation of *p*-dichlorobenzene (58.7 mol%) and hexachloroethane (38 mol%) indicates that homolysis is a major reaction. A comparison of the yields of *p*-dichlorobenzene and hexachloroethane ($38\times2-58.7=17.3$) indicates that a part of trichloromethyl radicals arose from the Cl-abstraction of carbon tetrachloride by radicals other than *p*-chlorophenyl radical. *p*-Chlorobenzoyloxy radical may be responsible for this, but it was not possible to isolate *p*-$ClC_6H_4CO_2Cl$, the product of such Cl-abstraction.

Of the four different cases of decomposition of CTP, that in benzene with suspended magnesium oxide is the most interesting, the decomposition being completely homolytic. This paper seems to be the first to describe the formation of a sulfonyloxy radical without competing side reactions.

Experimental

Materials. Benzene, carbon tetrachloride and *p*-toluenesulfonyl chloride were purified according to procedures described previously.[2] *p*-Chloroperoxybenzoic acid was prepared by the method used for the synthesis of *p*-nitroperoxybenzoic acid;[4] yield, 84.1%; mp 110—112°C (lit,[5] 111—113°C). Powdery magnesium oxide was heated in a crucible, cooled and then used.

Preparation of p-*Chlorobenzoyl* p-*Toluenesulfonyl Peroxide (CTP).* This new peroxide could not be prepared by the method used for the synthesis of benzoyl *p*-toluenesulfonyl peroxide. It was synthesized as follows. A solution of *p*-tosyl chloride (9.6 g, 0.05 mol) in dichloromethane (200 m*l*) was cooled to −22°C in a four-necked round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, a thermometer and a calcium chloride tube. Then, an aqueous 50% KOH solution (12 g) was added drop by drop with stirring. The temperature rose to some extent. After the solution was again cooled to −22°C, a solution of *p*-chloroperoxybenzoic acid (11.2 g, 0.06 mol) in dichloromethane (1 *l*) was added slowly while the temperature was kept below −20°C, it was washed with 10 *l* of ice water and dried over anhydrous magnesium sulfate. Evaporation of the dichloromethane under reduced pressure yielded a brownish residue, which gave colorless needles (9.3 g, 57%) upon recrystallization from ether. Recrystallization was repeated twice more and the crystals obtained were used for the experiments. They were stable for a long period at −20°C. Mp, 73—74°C (decomp). The main IR absorptions were observed at 1785, 1395, 1220, 1195, and 1180 cm^{-1}.

Found: C, 51.49; H, 3.17; Cl, 11.01; S, 9.68%. Calcd for $C_{14}H_{11}O_5ClS$: C, 51.46; H, 3.39; Cl, 10.85; S, 9.81%.

Kinetic Measurements. Rates of decomposition were measured by the procedure used for benzoyl *p*-toluenesulfonyl peroxide.[2] A 0.02 N $Na_2S_2O_3$ solution was used instead of a 0.05 N solution.

Analyses of Products of Decomposition. Products of decomposition of CTP were analyzed by a procedure essentially similar to that used in the case of benzoyl *p*-toluenesulfonyl peroxide. Since *p*-chlorophenyl *p*-toluenesulfonyl carbonate was found to decompose in a chromatographic column containing silica gel (Wako Gel Q22; 200 mesh), the reaction mixture was treated with aniline. When the mixture thus treated was subjected to elution chromatography, *p*-chlorophenyl *N*-phenylcarbamate produced was eluted with a hexane-benzene (1 : 2) mixed solvent.

Other products were determined by vapor phase chromatography. For determination of products from the decomposition in benzene, an Apiezon L column was used for *p*-chlorobiphenyl (internal standard, bibenzyl) and various esters (internal standard, *p*-tolyl benzoate). For determination of products in carbon tetrachloride, a silicone oil SE 30 column was used for *p*-dichlorobenzene and hexachloroethane (internal standard, *p*-dibromobenzene) and an Apiezon L column was used for various esters (internal standard, phenyl *p*-chlorobenzoate).

Preparation of p-*Chlorophenyl* p-*Toluenesulfonyl Carbonate.* *p*-Chlorophenyl chloroformate was prepared from *p*-chlorophenol and a 30% toluene solution of phosgene according to the method of Oesper *et al.*[6]; yield, 70.0%; bp 112.5—114°C/20 mmHg (lit,[6] 114°C/20 mmHg).

A solution of *p*-chlorophenyl chloroformate (2.8 g, 0.015 mol) and silver *p*-tosylate (4.2 g, 0.015 mol) in acetonitrile (50 m*l*) was refluxed for 10 hr. The silver chloride precipitated was filtered off, the acetonitrile was evaporated under reduced pressure, and recrystallization of the residue from ether-hexane yielded white crystals (3.1 g, 63.3%). Mp. 123—124°C. This mixed anhydride has not been reported in the literature. Its main IR absorptions were observed at 1785, 1395, 1245, and 1180 cm^{-1}.

Found: C, 51.37; H, 3.44; Cl, 10.58; S, 10.03%. Calcd for $C_{14}H_{11}O_5ClS$: C, 51.46; H, 3.39; Cl, 10.85; S, 9.81%.

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[4] M. Vilkas, *Bull. Soc. Chim. Fr.*, **1959**, 1401.

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[6] R. E. Oesper, W. Broker, and W. A. Cook, *ibid.*, **47**, 2609 (1925).